Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Revisiting the carbonyl $n \rightarrow \pi^*$ electronic excitation through topological eyes: expanding, enriching and enhancing the chemical language using electron number distribution functions and domain averaged Fermi holes

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Partition into $\Omega = \Omega_C \cup \Omega_H$ and $\Omega' = \Omega_O \cup \Omega_{H'}$

In this section, we show the decomposition of the EDF vector associated to the partition of formaldehyde into $\Omega_C \cup \Omega_H$ and its complement. Data correspond to the ground state (Table 1) and to the triplet T_1 state (Table 2), both described at a monodeterminantal level.

Table 1. Decomposition of the $\mathbf{p}_{16}$ EDF vector (with $\Omega = \Omega_C \cup \Omega_H$) into (2c,2e) links for the S_0 state (HF/cc-pVTZ). Each $\mathbf{p}_2$ vector presents a null f parameter and, consequently, only its q value is shown, together with the corresponding $\delta(\Omega, \Omega')$.

DNO	q_i	$\delta_i(\Omega,\Omega')$
$1s_O$	-1.0000	0.0000
$1s_C$	0.9981	0.0038
$2s_O$	-0.9990	0.0020
σ_{CH}	0.9366	0.1227
$\sigma_{CH'}$	0.0036	1.0000
σ_{CO}	-0.6782	0.5400
π_{CO}	-0.5813	0.6621
lp_O	-0.9467	0.1038

Table 2. Decomposition of the $\mathbf{p}_{16}$ EDF vector (with $\Omega = \Omega_C \cup \Omega_H$) into (2c,2e) links for the T_1 state (ROHF/cc-pVTZ). For each of these $\mathbf{p}_2$ vector, the triad (q, f, δ) is shown.

$\mathbf{p}_2^{ij} = \mathbf{p}_1(\phi_i) \otimes \mathbf{p}_1(\phi_j)$	(n_i^Ω, n_j^Ω)	q_{ij}	f_{ij}	$\delta_{ij}(\Omega,\Omega')$
$[1s_O]^\alpha \otimes [1s_O]^\beta$	(0.0000 , 0.0000)	-1.0000	0.0000	0.0000
$[1s_C]^\alpha \otimes [1s_C]^\beta$	(0.9990 , 0.9990)	0.9980	0.0000	0.0040
$[2s_O]^\alpha \otimes [2s_O]^\beta$	(0.0007 , 0.0007)	-0.9987	0.0000	0.0027
$[\sigma_{CH}]^\alpha \otimes [\sigma_{CH}]^\beta$	(0.9705 , 0.9340)	0.9045	0.0073	0.1806
$[\sigma_{CO}]^\alpha \otimes [\sigma_{CO}]^\beta$	(0.1562 , 0.1561)	-0.6878	0.0000	0.5270
$[\sigma_{CH'}]^\alpha \otimes [\sigma_{CH'}]^\beta$	(0.5282 , 0.5095)	0.0377	0.0003	0.9982
$[lp_O^\pi]^\alpha \otimes [lp_O]^\alpha$	(0.0147 , 0.0214)	-0.9639	0.0006	0.0709
$[lp_C^\pi]^\alpha \otimes [\pi_{CO}]^\beta$	(0.8551 , 0.1221)	-0.0229	0.5376	0.4622

Partition into $\Omega = \Omega_C \cup \Omega_O$ and $\Omega' = \Omega_H \cup \Omega_{H'}$

In this section, we consider the partition into $\Omega_C \cup \Omega_O$ and its complement (Tables 3 and 4).

Table 3. Decomposition of the $\mathbf{p}_{16}$ EDF vector (with $\Omega = \Omega_C \cup \Omega_O$) into (2c,2e) links for the S_0 state (HF/cc-pVTZ). Each $\mathbf{p}_2$ vector presents a null f parameter and, consequently, only its q value is shown, together with the corresponding $\delta(\Omega, \Omega')$.

DNO	q_i	$\delta_i(\Omega,\Omega')$
$1s_O$	1.0000	0.0000
$1s_C$	1.0000	0.0000
$2s_O$	0.9998	0.0004
$\sigma_{CH_2}(a1)$	0.2043	0.9583
$\sigma_{CH_2}(b2)$	-0.1369	0.9813
σ_{CO}	0.9925	0.0150
π_{CO}	0.9718	0.0556
lp_O	0.9874	0.0249

Table 4. Decomposition of the $\mathbf{p}_{16}$ EDF vector (with $\Omega = \Omega_C \cup \Omega_O$) into (2c,2e) links for the T_1 state (ROHF/cc-pVTZ). For each of these $\mathbf{p}_2$ vector, the triad (q, f, δ) is shown.

$\mathbf{p}_2^{ij} = \mathbf{p}_1(\phi_i) \otimes \mathbf{p}_1(\phi_j)$	(n_i^Ω, n_j^Ω)	q_{ij}	f_{ij}	$\delta_{ij}(\Omega,\Omega')$
$[1s_O]^\alpha \otimes [1s_O]^\beta$	(1.0000 , 1.0000)	1.0000	0.0000	0.0000
$[1s_C]^\alpha \otimes [1s_C]^\beta$	(1.0000 , 1.0000)	1.0000	0.0000	0.0000
$[2s_O]^\alpha \otimes [2s_O]^\beta$	(0.9999 , 0.9999)	0.9999	0.0000	0.0003
$[\sigma_{CH_2}]^\alpha \otimes [\sigma_{CH_2}]^\beta (a_1)$	(0.6170 , 0.6170)	0.2340	0.0000	0.9453
$[\sigma_{CO}]^\alpha \otimes [\sigma_{CO}]^\beta$	(0.9973 , 0.9973)	0.9945	0.0000	0.0109
$[\sigma_{CH_2}]^\alpha \otimes [\sigma_{CH_2} + \kappa \cdot lp_O]^\beta (b_2)$	(0.4727 , 0.5623)	0.0350	0.0080	0.9907
$[lp_O^\pi]^\alpha \otimes [lp_O]^\alpha$	(0.9996 , 0.9968)	0.9964	0.0011	0.0071
$[lp_C^\pi]^\alpha \otimes [\pi_{CO}]^\beta$	(0.9215 , 0.9960)	0.9174	0.0351	0.1527

Partition into $\Omega = \Omega_O$ and $\Omega' = \Omega_C \cup \Omega_H \cup \Omega_{H'}$

In this section, we consider the partition into Ω_O and its complement (Tables 5 and 6).

Table 5. Decomposition of the $\mathbf{p}_{16}$ EDF vector (with $\Omega = \Omega_O$) into (2c,2e) links for the S_0 state (HF/cc-pVTZ). Each $\mathbf{p}_2$ vector presents a null f parameter and, consequently, only its q value is shown, together with the corresponding $\delta(\Omega, \Omega')$.

DNO	q_i	$\delta_i(\Omega,\Omega')$
$1s_O$	1.0000	0.0000
$1s_C$	-0.9981	0.0037
$2s_O$	0.9988	0.0025
$\sigma_{CH_2}(a1)$	-0.9662	0.0665
$\sigma_{CH_2}(b2)$	-0.9183	0.1568
σ_{CO}	0.6678	0.5541
π_{CO}	0.5672	0.6783
lp_O	0.9251	0.1442

Table 6. Decomposition of the $\mathbf{p}_{16}$ EDF vector (with $\Omega = \Omega_O$) into (2c,2e) links for the T_1 state (ROHF/cc-pVTZ). For each of these $\mathbf{p}_2$ vector, the triad (q, f, δ) is shown.

$\mathbf{p}_2^{ij} = \mathbf{p}_1(\phi_i) \otimes \mathbf{p}_1(\phi_j)$	(n_i^Ω, n_j^Ω)	q_{ij}	f_{ij}	$\delta_{ij}(\Omega,\Omega')$
$[1s_O]^\alpha \otimes [1s_O]^\beta$	(1.0000 , 1.0000)	1.0000	0.0000	0.0000
$[1s_C]^\alpha \otimes [1s_C]^\beta$	(0.0010 , 0.0010)	-0.9981	0.0000	0.0039
$[2s_O]^\alpha \otimes [2s_O]^\beta$	(0.9992 , 0.9992)	0.9985	0.0000	0.0030
$[\sigma_{CH_2}]^\alpha \otimes [\sigma_{CH_2}]^\beta (a_1)$	(0.0134 , 0.0134)	-0.9732	0.0000	0.0528
$[\sigma_{CO}]^\alpha \otimes [\sigma_{CO}]^\beta$	(0.8385 , 0.8385)	0.6770	0.0000	0.5416
$[\sigma_{CH_2}]^\alpha \otimes [\sigma_{CH_2} + \kappa \cdot lp_O]^\beta (b_2)$	(0.0422 , 0.1369)	-0.8209	0.0275	0.3171
$[lp_O^\pi]^\alpha \otimes [lp_O]^\alpha$	(0.9843 , 0.9717)	0.9560	0.0019	0.0860
$[lp_C^\pi]^\alpha \otimes [\pi_{CO}]^\beta$	(0.1065 , 0.8759)	-0.0176	0.5923	0.4076

Partition into $\Omega = \Omega_{H'}$ and $\Omega' = \Omega_O \cup \Omega_C \cup \Omega_H$

In this section, we consider the partition into $\Omega_{H'}$ and its complement (Tables 7 and 8). Orbitals described by '—' are basically defined within Ω', but they are not identified with single bonds or lone pairs.

Table 7. Decomposition of the $\mathbf{p}_{16}$ EDF vector (with $\Omega = \Omega_{H'}$) into (2c,2e) links for the S_0 state (HF/cc-pVTZ). Each $\mathbf{p}_2$ vector presents a null f parameter and, consequently, only its q value is shown, together with the corresponding $\delta(\Omega,\Omega')$.

DNO	q_i	$\delta_i(\Omega,\Omega')$
$1s_O$	-1.0000	0.0000
$1s_C$	-1.0000	0.0000
$2s_O$	-0.9999	0.0001
—	-0.9872	0.0254
—	-0.9996	0.0007
$\sigma_{CH'}$	-0.0445	0.9980
—	-0.9923	0.0154
π_{CO}	-0.9859	0.0280

Table 8. Decomposition of the $\mathbf{p}_{16}$ EDF vector (with $\Omega = \Omega_{H'}$) into (2c,2e) links for the T_1 state (ROHF/cc-pVTZ). For each of these $\mathbf{p}_2$ vector, the triad (q, f, δ) is shown.

$\mathbf{p}_2^{ij} = \mathbf{p}_1(\phi_i) \otimes \mathbf{p}_1(\phi_j)$	(n_i^Ω, n_j^Ω)	q_{ij}	f_{ij}	$\delta_{ij}(\Omega,\Omega')$
$[1s_O]^\alpha \otimes [1s_O]^\beta$	(0.0000 , 0.0000)	-1.0000	0.0000	0.0000
$[1s_C]^\alpha \otimes [1s_C]^\beta$	(0.0000 , 0.0000)	-1.0000	0.0000	0.0000
$[2s_O]^\alpha \otimes [2s_O]^\beta$	(0.0000 , 0.0000)	-1.0000	0.0000	0.0001
$[-]^\alpha \otimes [-]^\beta$	(0.0054 , 0.0054)	-0.9892	0.0000	0.0215
$[-]^\alpha \otimes [-]^\beta$	(0.0002 , 0.0008)	-0.9990	0.0002	0.0019
$[\sigma_{CH'}]^\alpha \otimes [\sigma_{CH'}]^\beta$	(0.4505 , 0.4055)	-0.1440	0.0021	0.9772
$[lp_O^\pi]^\alpha \otimes [-]^\alpha$	(0.0002 , 0.0021)	-0.9977	0.0008	0.0046
$[lp_C^\pi]^\alpha \otimes [\pi_{CO}]^\beta$	(0.0393 , 0.0020)	-0.9587	0.0172	0.0795